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L8: Entry 2 of 5 File: USPT Feb 13, 2001

DOCUMENT-IDENTIFIER: US 6187519 B1
TITLE: Process and equipment for recovering developer from photoresist development waste and reusing it

BSPR:
Meanwhile, waste discharged from the development step of using an aqueous TAAH solution as the alkali developer in the photolithographic process (called "photoresist development waste" and hereinafter often referred to in brief as "development waste") usually contains the dissolved photoresist and TAAH, and is hard to render harmless through any treatments. Thus, it is desired to recover and reuse TAAH because of its adverse effects on environment, and various attempts have been made to develop a method of recovering and rejuvenating an alkali developer (hereinafter often referred to as "developer"). Examples of such a method include methods comprising electrodialysis or electrolysis (Japanese Patent Laid-Open No. 7-328642 published on Dec. 19, 1995, and Japanese Patent Laid-Open No. 5-17889 published on Jan. 26, 1993), a method using an anion exchange resin (Japanese Patent Laid-Open No. 10-85741 published on Apr. 7, 1998), a method comprising electrodialysis or electrolysis and using an ion exchange resin(s) (U.S. Patent No. 5,874,204 patented on Feb. 23, 1999), a method comprising neutralization and electrolysis (Japanese Patent Laid-Open No. 7-41989 published on Feb. 10, 1995), a method using activated carbon (Japanese Patent Laid-Open No. 58-30753 published on Feb. 23, 1983), and a method using a nanofiltration membrane (NF membrane) (Japanese Patent Laid-Open No. 11-192481 published on Jul. 21, 1999).

BSPR:
Various methods can be mentioned as the method of separating impurities such as photoresist from a development waste to recover a TAAH solution. Preferred is a method comprising subjecting the development waste to at least one step selected from among a concentration and refining step (A) of concentrating and refining TAAH by at least one of electrodialysis and electrolysis (Japanese Patent Laid-Open No. 7-328642 and Japanese Patent Laid-Open No. 5-17889, incorporated herein by reference in their entirety), an ion exchange treatment step (B) of contact treatment with an anion exchanger (preferably an anion exchange resin desirably in the OH form in an aspect of refining) or with the above-mentioned anion exchanger and a cation exchange resin in one of the H form and the TAA form (Japanese Patent Laid-Open No. 10-85741 and U.S. Pat. No. 5,874,204, incorporated herein by reference in their entirety), and an NF membrane separation treatment step (C) of obtaining permeate mainly containing TAAH by treatment with a nanofiltration membrane (NF membrane) [Japanese Patent Laid-Open No. 11-192481, incorporated herein by reference in its entirety once laid open although it has not yet been published]. When a plurality of such steps are taken, the order thereof may be arbitrary, and any proper order thereof may be chosen, for example, in accordance with the purpose. The steps (A), (B) and (C) can all remove impurities as steps of refining the development waste or a TAAH containing treated solution derived therefrom. Among them, the step (B) in particular is a desirable step for removing impurities as much as possible, and the step (A) can concentrate TAAH.

BSPR:
Examples of the NF membrane that may be used in the step (C) include NTR-7410, NTR-7450, NTR-729HF, NTR-7250, NTR-729HF, and NTR-769SR manufactured by NITTO DENKO CORPORATION; SU-200S, SU-510, and SU-610 manufactured by Toray Industries, Inc.; NF-45, NF-85, NF-70, and NF 90 manufactured by FilmTec Corporation; DESAL-5L and DESAL-5K manufactured by Desal Co. Limited; TS-80 manufactured by TriSep Corporation; TFC-S manufactured by Fluid Systems; and MPF-34, MPF-36,

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L14: Entry 5 of 6 File: USPT May 12, 19..

DOCUMENT-IDENTIFIER: US 5112483 A
TITLE: Slow sand nanofiltration water treatment system

BSPR:
The prefix nano means one thousand millionth or 10.sup.-9. One nanometer is equivalent to 10 angstroms. The NF-70 NANOFILTRATION membranes made by FilmTec, a subsidiary of Dow Chemical Company, will reject all molecular species of 10 angstroms or greater in diameter consistent with a 200 molecular weight cutoff. Rejection of molecular species below a 200 molecular weight is dependent on their size, ionic charge and membrane affinity. This molecular weight cutoff is ideal for eliminating organic precursors that are not removed in conventional water treatment plants. These nanofilters will remove most of the sulfate, calcium and magnesium products in the water and about 1/2 of the sodium and chloride compounds. Other companies, including Desal, make a similar type of membrane.

MPT-34, MPT-36, MPS-34 and MPS-36 of Sel RO registered trademark [illegible]
manufactured by Koch Membrane Systems, Inc.

BSPR:
An NF membrane having a surface thereof charged negative is preferably used as a
membrane principally aimed at separation and removal of photoresist into the
concentrate. Since the photoresist usually exists in the anionic form in the
development waste or the TAAH-containing treated solution derived therefrom
(e.g., TAAH-containing solution treated in the step (A) and/or (B)), the use of
the NF membrane having a surface thereof charged negative improves the rejection
against the photoresist and hardly brings about fouling (contamination) of the NF
membrane otherwise attributed to attachment thereto of the photoresist. In this
case, an anionic surfactant, when contained in the development waste or the
TAAH-containing treated solution derived therefrom, can also be effectively
separated and removed into the concentrate. Further, in general, the NF membrane
is also capable of separating and removing a nonionic surfactant, a cationic
surfactant, etc. into the concentrate. Needless to say, an NF membrane having a
surface thereof charged positive or a neutral NF membrane may also be used in
accordance with properties of the development waste or the TAAH-containing
treated solution derived therefrom (e.g., the kind of surfactant, if contained
therein). The concentrate containing the photoresist and/or a surfactant and thus
separated with the NF membrane may be used as a source of surface-active
substance either as such or after proper refining treatment thereof such as ion
exchange resin treatment and/or chelate resin treatment if necessary.

CLPR:
3. A process for recovering a developer from a photoresist development waste and
reusing it as claimed in claim 1, wherein the method of separating impurities
including photoresist from a photoresist development waste for recovering a
tetraalkylammonium hydroxide solution comprises subjecting the photoresist
development waste to at least one step selected from the group consisting of a
step (A) of concentrating and refining tetraalkylammonium hydroxide by at least
one of electrodialysis and electrolysis, a step (B) of contact treatment with an
anion exchange resin and/or a cation exchange resin in one of the H form and the
tetraalkylammonium ion form (TAA form), and a step (C) of obtaining permeate
mainly containing tetraalkylammonium hydroxide by treatment with a nanofiltration
membrane (NF membrane).

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